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Lubricity from Entangled Polymer Networks on Hydrogels

Structural hydrogel materials are being considered and investigated for a wide variety of biotribological applications. Unfortunately, most of the mechanical strength and rigidity of these materials comes from high polymer concentrations and correspondingly low polymer mesh size, which results in high friction coefficients in aqueous environments. Recent measurements have revealed that soft, flexible, and large mesh size hydrogels can provide ultra low friction, but this comes at the expense of mechanical strength. In this paper, we have prepared a low friction structural hydrogel sample of polyhydroxyethyl-methacrylate (pHEMA) by polymerizing an entangled polymer network on the surface through a solution polymerization route. The entangled polymer network was made entirely from uncrosslinked polyacrylamide (pAAm) that was polymerized from an aqueous solution and had integral entanglement with the pHEMA surface. Measurements revealed that these entangled polymer networks could extend up to $\sim 200 \mu\text{m}$ from the surface, and these entangled polymer networks can provide reductions in friction coefficient of almost two orders of magnitude ($\mu > 0.7$ to $\mu < 0.01$). [DOI: 10.1115/1.4032889]

Keywords: friction, hydrogel, entangled polymer network, lubricity, mesh size

1 Introduction

In Frederick F. Ling's text on Surface Mechanics, he derived the solution for the pressure distribution that resulted during contact and sliding on thin elastic or viscoelastic layers that were integrally attached to an elastic half-space [1,2]. Under conditions in

which these layers are thin relative to the contact width, the resulting solutions are extremely close to the predictions made by classical theories that do not account for these layers. While these thin, soft layers do not excessively alter the contact pressures or contact conditions, they may still fundamentally change the friction by altering the surface chemistry and morphology of the contacting interface [3].

The use of strong elastic hydrogel materials such as polyvinyl alcohol and pHEMA for biological replacement tissues is currently an active area of research [4–17]. Most of these strong

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hydrogel materials achieve their strength and stiffness by having relatively low polymer mesh size ($\xi < 2$ nm) and correspondingly high polymer concentrations. Recently, Uruña et al. have shown that mesh size is directly related to friction coefficient in Gemini hydrogel systems [18]. The model that emerges from this work is that the fluctuating solvated polymer chains at the surface allow for easy shearing of the solvent through the contact area and thus provide low friction. Under conditions in which the contact pressure does not collapse the gel network, the amplitude of polymer fluctuations is significantly large enough to keep the surfaces separated and not restrict the flow of the shearing solvent [19,20].

For tough, low mesh size hydrogels, the thermal fluctuations are small, and the friction coefficients under aqueous conditions are often prohibitively high with many materials having friction coefficients over $\mu > 0.7$ [16]. Of interest here is whether or not the creation of entangled polymer networks off of these surfaces can provide low friction by having an open mesh size at the sliding interface, while simultaneously retaining the structural strength of the underlying hydrogel. In this paper, we have synthesized a gradient of entangled polymer networks of pAAm that were polymerized from the subsurface of pHEMA substrates by making a gradient in immersion time in an acrylamide solution. The resulting gradient in the entangled polymer network properties and thickness provided an opportunity to perform high-throughput analysis, and also provides a straightforward route to create open mesh size polymer entangled networks on hydrogel materials [21].

2 Materials and Methods

Hydrogel substrates were prepared by polymerizing the following components reported as mass-per-mass of solvent: HEMA monomer (67%), N,N'-methylenebisacrylamide crosslinker (0.2%), ammonium persulfate (APS) (0.1%), tetramethylethylenediamine (TEMED) (0.01%) in ultrapure water and in an oxygen-deprived environment at 60 °C for 40 mins. To enable optical measurements of the pHEMA surface, a 0.1% concentration of 2 μ m tint particles were dispersed in the polymerization mix before gelling. Polymerization was performed by casting the precursor solution between glass plates and cutting the pHEMA gel into flat rectangular sheets with dimensions of 75 \times 25 \times 5 mm.

Acrylamide polymers entangled within the subsurface region of pHEMA substrates and emanating outward into bulk solution were generated by a dip polymerization method shown in Fig. 1(a). The method employs concentration gradients in catalyst and monomer across the pHEMA surface to initiate acrylamide polymerization within the pHEMA substrate. A catalyst gradient was achieved by soaking one of the 75 \times 25 mm faces of the pHEMA substrate in a 50% TEMED solution for 10 mins. After soaking, the excess solution was dabbed away from the surface with lens paper and rinsed with ultrapure water. The whole pHEMA slab was then rapidly dipped into a 45 mL container of 10% acrylamide monomer and 0.25% APS solution in ultra-pure water and retracted at a constant rate, setting a spatially varying immersion time for acrylamide polymerization along the pHEMA substrate. A computer-controlled servo motor stage was used to perform this controlled immersion time of the hydrogel into the acrylamide bath (Fig. 1(a)) at retraction rates of 0.1 or 1 mm/s. Immersion times for controlled acrylamide polymerization and growth varied from \sim 5 s to 400 s. The thickness of the pAAm networks grown on the pHEMA substrates was expected to increase with growth time (Fig. 1(b)).

Optical microscopy was used to measure the thickness of the pAAm surface layer. The pHEMA sample was placed pAAm-side down on a glass microscope slide (\sim 1 mm in thickness) mounted on an inverted microscope. The apparent thickness, t_a , of the pAAm surface network was determined from the location of the glass slide top surface and from the location of the lowest plane of particles embedded in the pHEMA measured along the optical

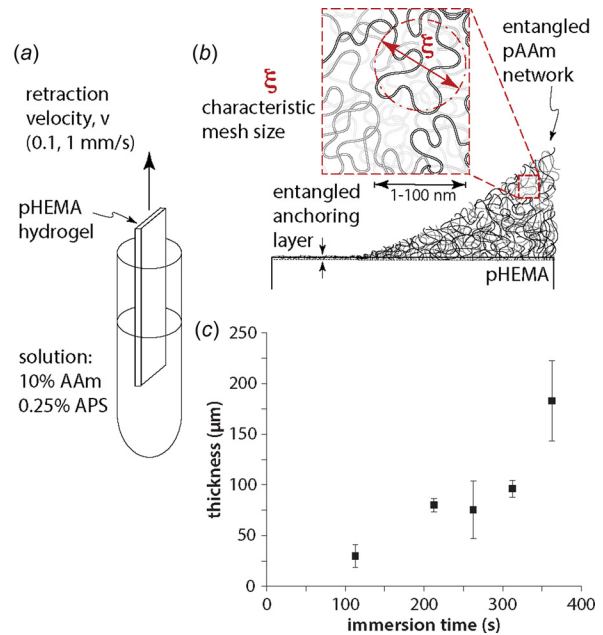


Fig. 1 (a) Hydrogel samples were prepared by polymerizing a 67% pHEMA substrate soaking these samples in a 50% TEMED solution for 10 min. Samples were submerged in a bath of 10% acrylamide solution and retracted immediately at a prescribed velocity. Entangled pAAm networks grew from within and extended out of pHEMA substrate as it was slowly drawn out of the solution. (b) Illustration of entangled, high water content pAAm networks grown onto the pHEMA substrate. (c) Increasing polymerization time yields increasing surface layer thickness. Microscopy revealed that the thickness of these entangled polymer networks increased with increasing time in the acrylamide solution. Error bars represent the standard deviation of the measured thickness over five different regions along the width of the sample.

axis. To calculate the real thickness, t_r , the apparent thickness was corrected for refractive index mismatching and the numerical aperture of the objective by the following equation:

$$t_r = t_a \left(\frac{n_w^2 - NA^2}{n_a^2 - NA^2} \right)^{1/2} \quad (1)$$

where n_w and n_a are the refractive indices of water and air, respectively, and NA is the numerical aperture of the objective. Five thickness measurements were performed in five locations along the length of the pHEMA sample to get an average thickness measurement and corresponding standard deviation.

Microtribological measurements of the surface gel layers were performed using a custom-built microtribometer described previously [22,23]. A double titanium flexure with normal and tangential force constants of 85 μ N/ μ m and 70 μ N/ μ m, respectively, was used to apply and measure normal (F_n) and resulting friction (F_f) forces. Capacitive sensors (5 μ m/V sensitivity and 20 V range) mounted axially and tangentially to the probe were used to measure displacements. The coefficient of friction, μ , was computed as the ratio of the measured friction force to the normal force for the free sliding region of each reciprocating cycle. Uncertainty in friction measurements is discussed by Schmitz et al. [24].

A hemispherical borosilicate glass probe (3.1 mm radius of curvature) was slid against all hydrogel samples with a reciprocating stroke length of 800 μ m, sliding velocity of 200 μ m/s, and nominal normal load of 750 μ N. Friction experiments were performed sliding widthwise at multiple locations along the length of the

pHEMA hydrogel to investigate the effects of soak time on gradient a pAAm surface layer thickness and lubricity.

3 Results and Discussion

Upon removal from the acrylamide solution, the pHEMA slabs were slippery to the touch and presented handling challenges and this persisted after the pHEMA slabs were equilibrated in water for over 24 hrs. Another indication that a robust entangled polymer network was formed on the surface of these hydrogels was that samples intentionally immersed on only one side were found to bend into different curvatures depending on immersion time and solvents. We also observed that the immersion bath became a viscous polymer solution during the sample retraction process. This result is a natural consequence of the expanding front of the TEMED concentration profile that diffuses from the pHEMA slab.

Direct measurements of the layer thickness are challenging for transparent high water content hydrogel and polymer networks. The thickness of the largest pAAm surface network was measured by fluorescence microscopy to be approximately $200\ \mu\text{m}$ after an immersion time of 400 s. However, it is highly unlikely (if not outright impossible) that any single chain could be $\sim 200\ \mu\text{m}$ in length. The layer must consist instead of smaller entangled chains, each approximately a few million molecular weight and $\sim 100\ \text{nm}$ in length. Furthermore, the overlap concentration, C^* , of this polymer solution is 0.5% thus chains are $\sim 95\ \text{nm}$ long meaning that the thickness of this layer comes from the overlap and entanglement of many, many chains [25,26]. The region of pHEMA submerged for the shortest amount of time in the pAAm solution had a surface region about $10\ \mu\text{m}$ in thickness. The entangled polymer network thickness increased monotonically with immersion time in the pAAm bath (Fig. 1(c)).

These thick polymer entangled networks were made from pAAm without any crosslinking functionality. However, these layers are sufficiently robust to support contact pressures on the order of 10 s of kPa and under testing at a contact load of $750\ \mu\text{N}$, these surfaces had outstanding lubricity, with friction coefficients of the short immersion times being below $\mu < 0.01$ (Fig. 2). In comparison, the friction coefficient of the untreated pHEMA surfaces against a glass probe was measured to be $\mu = 0.720 \pm 0.047$ and a homogeneous crosslinked sample of pAAm at 10% concentration of polymer was found to be

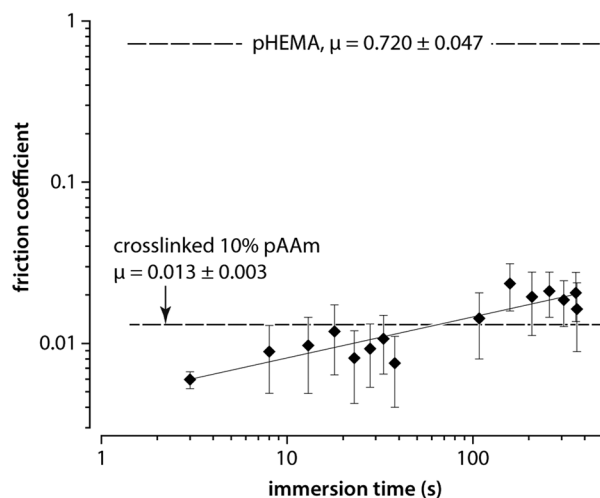


Fig. 2 Friction coefficient as a function of pHEMA immersion time in the acrylamide bath. Ultra low friction coefficients, $\mu < 0.01$, were observed at the shortest immersion times and correspondingly thinnest layers. Error bars represent the standard deviation of the measured friction coefficient over the last 40 reciprocating cycles.

$\mu = 0.013 \pm 0.003$. This pAAm entangled polymer network surface not only dramatically reduced the friction coefficient of pHEMA hydrogels but was also robust to extended sliding cycles. Our experiments, which report an average value for friction coefficient, were performed over 50 times on each location.

4 Concluding Remarks

We have presented an easy and accessible method to produce low friction surfaces by polymerizing uncrosslinked long chains into entangled polymer networks on hydrogel surfaces. The absence of a crosslinker during polymerization can only result in the creation of long chain, highly entangled polymers. In fact, the remaining monomer solution from the dip experiment turned from an aqueous solution to a honeylike viscous gel. Based on our thickness measurements, these polymer chains must form an entangled network on the surface of the pHEMA sheet. Lubricity measurements confirm the existence of this network due to persistent low friction coefficients over 50 reciprocating sliding cycles. Under low contact pressure conditions, friction coefficients were reduced from high friction characteristic of pHEMA ($\mu > 0.7$) to ultra low values of $\mu < 0.01$.

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